

RESEARCH ARTICLE

Recycling of a Polymer Mixture Through Dissolution–Precipitation and Development of Machine Learning Models to Assess Polymer/Solvent Suitability

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ABSTRACT

Different plastics require specific recycling methods, but mixing various types can complicate their recycling together. In this study, an innovative method for recycling mixed plastics was developed, based on the principle of dissolution–precipitation, focusing on a plastic mixture typically found in plastic recycling bins. Initially, different solvents were employed to dissolve polymers individually being the dissolution extent determined. Using this data, together with solubility parameters, including the Hildebrand coefficients and others, of both the plastics and solvents, were used as inputs to develop machine learning (ML) models. These models aimed to identify solvents with suitable properties for dissolving specific polymers. The developed model achieved a training accuracy of 92.03% and a testing accuracy of 84.62%. However, when examining other, often more meaningful metrics, Precision, Recall, and F1-Measure scores of 42.31%, 50%, and 45.83%, respectively, were obtained. Despite these preliminary challenges, this stage laid the groundwork for developing a methodology capable of isolating all polymers present in a mixture with high selectivity (between 93.5% and 108.7%). The recovered polymers exhibited identical chemical, thermal, and mechanical properties to their original counterparts. Overall, this work provides a pathway toward a more sustainable and circular approach to managing plastic waste.

1 | Introduction

Polymers, commonly referred to as plastics, find extensive applications across diverse sectors such as household appliances, packaging, construction, electronics, automotive, and more. Their adaptability in processing and the capacity to tailor their properties make them massively used. However, a major drawback lies in the fact that polymers are not easily recyclable, leading to their disposal in landfills or incineration after use [1, 2]. In

fact, the world generates over 350 million metric tons of plastic waste annually, and without alterations to existing policies, projections indicate that global plastic waste generation will triple by 2060, reaching a staggering 1 billion metric tons [3].

As we utilize various types of plastic products daily, they are disposed of in plastic recycling bins. Hence, municipal plastic wastes are typically composed of a mix of plastics with varying composition, including 23% of low-density polyethylene

(LDPE), 19% of high-density polyethylene (HDPE), 14% of polypropylene (PP), 10% of polyethylene terephthalate (PET), 9% of polystyrene (PS), 6% of polyvinyl chloride (PVC), and 19% of others, such as polyurethane (PU) [4]. This intricate composition is a primary obstacle to their valorization, contributing to the prevalent disposal of plastics in landfills or incineration. The imperative for finding an effective and comprehensive solution for plastic recycling is crucial to achieving environmental sustainability. In response to this, significant strides have been taken in the development of recycling technologies for polymer wastes [5, 6].

A method for recycling plastic waste is dissolution–precipitation [7]. In this dissolution–precipitation process, polymer waste undergoes dissolution in a solvent, followed by a filtration step to remove undissolved contaminants such as dirt, filters, other polymers, etc. The dissolved polymer can be subsequently recovered as a pure resin through three methods: (1) the addition of an anti-solvent; (2) evaporating the solvent from the polymer solution; (3) reducing the temperature of the polymer solution to recover the polymer as a precipitate [8, 9].

The dissolution–precipitation recycling process has been employed successfully for recovering various types of polymers [8, 10–14]. The solubility of polymers is influenced by internal energy interactions and several key factors [15, 16]: (i) polarity (the interaction between polymer chains and solvent molecules depends on their polarity); (ii) intermolecular forces (strong dipole–dipole or hydrogen bonding interactions can hinder the penetration of solvent molecules between polymer chains); (iii) crystallinity (more crystalline polymers are more difficult to dissolve). In simple terms, similarity in chemical structure between the polymer and the solvent enhances solubility; (iv) chain structure (linear chains, being more entangled, are harder to dissolve compared to branched chains of similar molecular weight); (v) molecular weight (polymers with higher molecular weight are more difficult to solvate); or (vi) temperature (generally, as temperature increases, the solubility of a polymer in a solvent also increases). The dielectric characteristics of both polymers and solvents are crucial for the solubility of polymers in solvents [17]. The dielectric constant, a measure of material polarity, governs solubility by the “like dissolves like” principle: polar polymers favor polar solvents, while non-polar polymers favor non-polar solvents. Matching dielectric constants enhances favorable interactions, dipole–dipole interactions, and solubility. High dielectric constants in solvents stabilize charged or polar groups on polymers, promote ionic species dispersion, and enable hydrogen bonding with suitable functional groups. Thermodynamically, aligning dielectric properties minimizes mixing enthalpy, making Gibbs free energy more negative and solubility favorable. Similarly, the Hansen solubility parameters serve as a predictive tool for determining whether a material will dissolve in a particular solvent or solvent mixture [18].

Other methods based on solubility principles, such as solvent-targeted recovery and precipitation (STRAP), can be used to recycle polymers. STRAP is a specialized technique for selective polymer recovery from complex waste streams, while dissolution–precipitation is a more general method for polymer separation and purification. The STRAP method has been applied to separate polymers in plastic waste streams by selective

dissolution for recycling multilayer plastic packaging materials [19] and deconstructing multilayer films into their constituent resins [12]. Furthermore, the use of solvent mixtures can enhance polymer dissolution and recovery rates, as shown in Hanschmann's study [13], which explored solvent mixtures for the dissolution and precipitation of PP and PET. The application of machine learning (ML) to evaluate solvent blend performance is also promising.

In fact, ML has been shown to be effective quickly in identifying solvents that can or cannot dissolve polymers [20] even for predicting polymer solubility in solvents across concentrations and temperatures [21]. Therefore, in this work, a combination of the previously mentioned parameters and the results of physical experimentations was used to build and test different ML algorithms and their feasibility, aiming to identify the best solvents to dissolve a given polymer [22, 23]. Several algorithms were tested using a Grid Cross-Validation [24] approach to find the best fitting model, having the results from the algorithms guide future physical experiments instead of a trial-error approach, which is a lot more time- and resource-consuming. Overall, with the primary goal of contributing to the reduction of the environmental impact of the plastic sector, this work is dedicated to developing a recycling methodology that facilitates polymer recovery.

2 | Materials and Methods

2.1 | Materials

Pellets of Polystyrene (PS) with an average molecular weight of $350,000\text{ g mol}^{-1}$ were supplied by Sigma-Aldrich; Polyvinyl chloride (PVC) plasticized using circa 70 phr (parts per hundred of resin) of biobased plasticizer was kindly supplied by Compogal—Indústria de Polímeros, S.A. Pearlthane 11H94 is a polycaprolactone copolyester-based thermoplastic polyurethane (TPU) was supplied by Lubrizol; LDPE was supplied by Sigma-Aldrich; HDPE (flush) was supplied by 3devo; PP with an average molecular weight of $340,000\text{ g mol}^{-1}$ was supplied by Sigma-Aldrich; PET was supplied by Sigma-Aldrich. Ketone was supplied by Fisher; Acetonitrile (AcetoN) was supplied by Merck; Chloroform (ChloroF) was supplied by Panreac; Dichloromethane (DichloroM) was supplied by Fisher; Dimethylformamide (DMF) was supplied by Fisher; Dimethyl sulfoxide (DMSO) was supplied by Fisher; Hexane was supplied by Fisher; 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was supplied by Thermo Scientific; Tetrahydrofuran (THF) was supplied by Fisher; Toluene was supplied by Fisher; Xylene was supplied by Sigma-Aldrich; All solvents used were PA grade, and both polymers and solvents were used as received.

2.2 | Solubility of Polymers

In preliminary tests, different types of polymers were dissolved in different solvents in glass containers at ambient temperature, using a solvent/polymer ratio (v/wt) of 50 for 30 min under magnetic stirring (150 RPM). The exceptions were the dissolution of TPU, in which a solvent/polymer ratio (v/wt) of 100 was used; the dissolutions of LDPE, HDPE, and PP, in which xylene at

85°C, 110°C, and 135°C was used respectively (no dissolution occurred at room temperature). The conditions used were established based on prior knowledge and insights from the literature. After the dissolution, the solid fractions (if any) were separated from the liquid fraction via decantation. Finally, the solvents were evaporated from the liquid fraction using a ventilated oven at 60°C–80°C overnight (circa 12 h). The solubility/extraction of polymers ($\%_{\text{solubility}}$) was determined using equation (1).

$$\%_{\text{solubility}} = \frac{m_{\text{initialpolymer}} - m_{\text{dissolvedpolymer}}}{m_{\text{initialpolymer}}} \times 100 \quad (1)$$

where $m_{\text{dissolvedpolymer}}$ is the mass of polymers present in the liquid fraction and $m_{\text{initialpolymer}}$ is the initial mass of polymers.

After preliminary tests, a methodology was established to recycle a mixture of plastics, consisting of polymers commonly found in plastic recycling bins (equal mass proportions were used).

2.3 | Machine Learning

Based on the results from the earlier experiments, various combinations of solvents and polymers were utilized to develop an ML model intended to guide future experimental endeavors. A dataset was built with the results of each combination of polymer and solvent. The input variables that compose the model feature vector are: Polarity, Dielectric Constant, Hansen Parameters (Dispersion δD , Polarity δP , Hydrogen Connections δH , Hansen Parameter), Hildebrand Parameter, Flory Huggins parameter, Surface Energy, Van der Waals volume, Refraction Index, Gibbs Free Energy, and the Contact Angles coefficients. In addition, the extraction of each polymer was converted into a classification problem, where solubilities higher than 80% were considered successful. After data clean up, 63 data points were obtained, of which 12 were considered positive (extent of solubility over 80%, labeled as 1) and 51 were negative (labeled as 0).

Different ML algorithms were tested (Random Forest, Decision Tree, K-Nearest Neighbors (KNN), Neural Network, Gaussian Naive Bayes and Support Vector Machines (SVM)) using a method called Grid Search Cross Validation [24] for parameter optimization. For this method, and to ensure meaningful results, the data between Test and Train (80% for training, 20% for testing) was split using a stratified approach (the ratio between positive and negative classes is kept similar to the real data). The metrics used to evaluate the models were Accuracy, Precision, Recall, and F1-Measure. To better understand the results and visualize the data points from the physical experiments, a further study was also done using t-SNE.

2.4 | Characterization

The FTIR spectra were collected on a Perkin Elmer FTIR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. All data were recorded at room temperature, in the range 4000–500 cm^{-1} , by accumulating 32 scans with a resolution of 4 cm^{-1} .

Raman spectra were acquired using a Raman-AFM-SNOM WITec alpha300RAS+ confocal spectrometer. A Nd:YAG laser operating at 532 nm was used as an excitation source.

^{13}C solid-state Cross Polarization-Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C CPMAS NMR) spectra were recorded on a Bruker Avance 400 spectrometer. Samples were packed into a zirconias rotor sealed with Kel-FTM caps and spun at 12 kHz. Acquisition parameters were as follows: ca 7000 scans with a 90 proton pulse, a cross-polarization contact time of 1 ms, and a recovery delay of 2.5 s.

X-ray diffraction (XRD) patterns were collected using a Philips X'pert MPD diffractometer (Eindhoven, Netherlands) with Cu $K\alpha$ radiation. The scattered radiation was detected in the angular range from 5° to 50° (2θ).

Differential scanning calorimetric (DSC) analyzes were carried out in a single heating cycle using a Netzsch DSC 204F1 Phoenix at a heating rate of 10 °C min^{-1} .

Dynamic mechanical analyzes (DMA) were carried out using a Tritec 2000 equipment (Triton Technologies). Samples were analyzed in tension mode at a constant heating rate of 2 °C min^{-1} and at a frequency of 1 Hz. The glass transition temperatures (T_g) were measured at the top of the $\tan(\delta)$.

Thermogravimetric analysis (TGA) was performed using a SETSYS Evolution 1750 thermogravimetric analyzer (Setaram) from room temperature up to 800°C, at a heating rate of 10 °C min^{-1} and under nitrogen flux (200 mL min^{-1}).

3 | Results and Discussion

3.1 | Solubility of Polymers Using Different Solvents

The selective recycling of a mixture of different polymers began with preliminary tests to evaluate suitable solvents for each type of polymer being the results listed in Table 1.

As mentioned, the solubility of a polymer in a solvent depends on various factors, including polarity and intermolecular forces. Solvents with a high dielectric constant effectively dissolve polar and ionic substances by stabilizing ions and polar molecules through electrostatic interactions. Conversely, solvents with a low dielectric constant are more suitable for dissolving non-polar substances like hydrocarbons, where London dispersion forces predominate over dipole–dipole interactions. Therefore, solvents such as DMF, DMSO, or acetone are good candidates for dissolving PVC and TPU, while solvents like Toluene, Hexane, or Xylene are effective for dissolving LDPE, HDPE, and PP. The results presented in Table 1 support these claims. DMF showed a high extent of dissolution when used to dissolve PS or TPU, while xylene demonstrated a high extent of dissolution for PS, LDPE, HDPE, and PP.

However, the dielectric constant alone does not identify good solvents for polymers. If it did, Ketone would dissolve PVC or TPU, and Hexane would dissolve LDPE, HDPE, and PP,

TABLE 1 | Solubility of polymers using different solvents.

	Ketone	AcetoN	ChloroF	DichloroM	DMF	DMSO	Hexane	HFIP	PEther	THF	Toluene	Xylene
PS	0.8%	0.6%	99.8%	93.0%	98.6%	0.4%	0.5%	0.5%	0.1%	99.8%	98.0%	99.3%
PVC	16.7%	3.0%	16.6%	95.1%	50.0%	3.0%	8.0%	11.7%	7.2%	94.2%	5.9%	40.3%
TPU	1.0%	0.6%	0.9%	1.7%	97.2%	35.0%	0.7%	97.5%	0.1%	3.2%	0.3%	5.6%
LDPE	0.8%	1.6%	1.7%	4.4%	1.1%	3.0%	1.8%	1.8%	1.8%	1.5%	1.7%	97.3% ^a
HDPE	4.3%	0.7%	1.5%	1.9%	1.4%	2.5%	1.6%	1.6%	1.1%	1.5%	1.7%	82.9% ^b
PP	0.7%	0.4%	0.5%	0.8%	0.3%	10.8%	0.6%	0.4%	10.8%	0.3%	0.3%	99.6% ^c
PET	4.3%	0.6%	0.6%	0.8%	0.2%	0.1%	1.2%	92.3%	0.0%	0.4%	0.5%	3.6% ^a

^aDissolution carried out at 85°C.

^bDissolution carried out at 110°C.

^cDissolution carried out at 135°C.

which was not the case. Hence, for further identification of good polymer/solvent pairs, their Hansen parameters were analyzed. These parameters, which are listed in the Supporting Information (Table S1), give information about the polarity and intermolecular bonds of polymers and solvents. Hansen parameters consider three main components: dispersion forces (δd), polar forces (δp), and hydrogen bonding forces (δh). The effectiveness of these parameters in predicting solubility lies in their ability to match the cohesive energy density of the polymer with that of the solvent. In other words, solvents with Hansen parameters closely matching those of the polymer are more likely to dissolve it. For instance, polar polymers dissolve better in solvents with similar δp values, as seen with DMF and TPU, whereas non-polar polymers prefer solvents with matching δd values, as seen with xylene and PP.

Other properties of solvents, such as molecular weight, molecular structure, and crystallinity, influence their solubility. Generally, as the molecular weight increases, the solubility decreases. In terms of structure, branched polymers tend to be more soluble than their linear counterparts because branching reduces chain packing and entanglement, making it easier for solvent molecules to penetrate and interact with the polymer chains. Cross-linked polymers are generally insoluble because the network structure prevents the polymer chains from disentangling and interacting freely with the solvent. They may swell in a solvent but not dissolve completely. Since information about the molecular weight and structure of the polymers is not available, the effect of these characteristics on their solubility will not be discussed.

Overall, it was demonstrated that the dissolution of polymers in solvents is dependent on many factors. Yet, the results presented in Table 1 are supported by literature. García et al. [25] investigated the solubility of PS wastes in a dissolution recycling process using various solvents, including benzene, Toluene, Xylene, THF, chloroform, 1,3-butanediol, 2-butanol, DMF, and water. It was reported that PS was soluble in solvents such as Benzene, Toluene, Xylene, THF, chloroform, and DMF. These findings align with the results presented in Table 1, where PS exhibited a high solubility in chloroform, dichloromethane, DMF, THF, Toluene, and Xylene. Moreover, the solubility of a polymer in solvents is influenced by polarity. PS tends to dissolve better in non-polar solvents, which are chemically and physically similar to it. However, polar solvents can also be used in the recycling process if they do not have a strong tendency to form hydrogen bonds.

Regarding the solubility of PVC, higher solubilities were observed when using DichloroM or THF. Lapčík et al. [26] conducted a kinetic study on the dissolution of PVC in THF, cyclohexanone, cyclopentanone, and DMF. Their comparison of the activation energy values for diffusion established the following order of solvents by decreasing effectiveness in dissolving PVC: THF > cyclohexanone > cyclopentanone > DMF. These results were attributed to the lower kinetic activity of DMF, which is explained by its higher tendency to form molecular associations (indicated by a higher boiling point) and greater spatial shielding of charge vacancy. More recently, Grause et al. [27] used solubility parameters to identify optimal solvents for separating PVC from PVC-coated PET fibers. They

found that THF, cyclohexanone, and cyclopentanone were effective in dissolving PVC.

TPU exhibits a widely varying response to different media. According to Covestro [28], thermoplastic TPU swells slightly in saturated hydrocarbons such as diesel oil, isooctane, petroleum ether, and kerosene. Aromatic hydrocarbons like benzene and toluene cause pronounced swelling in TPU, as well as ketones such as acetone, MEK, and cyclohexanone. In contrast, polar organic solvents such as DMF, DMSO, N-methylpyrrolidone, and THF dissolve thermoplastic TPU. Analyzing the results in Table 1, only DMF and HFIP completely dissolved the TPU sample. The different behavior regarding solubility in polar solvents can be attributed to the composition of TPU, specifically its soft and hard segments. Gallu et al. [29], in her study on the use of solubility parameters to investigate phase separation of TPU, demonstrated that overall TPU solubility strongly decreases with increasing hard segment content.

LDPE, HDPE, and PP share a similar chemical structure, resulting in comparable properties. These polymers generally exhibit low solubility in most solvents at room temperature; hence, solvent mixtures and/or high temperatures are commonly used to dissolve them. Hadi et al. [30] explored the applicability of the dissolution/precipitation technique for recycling commercial LDPE, HDPE, and PP using various solvents and temperatures. Their results showed that a mixture of Toluene and PEther achieved high recovery extents of LDPE at 70°C, HDPE at 98°C, and PP at 101°C. Pappa et al. [10] also employed the selective dissolution/precipitation technique for recovering LDPE/PP mixtures, reporting high recovery extents for LDPE at 85°C and PP at 135°C using Xylene as the solvent. These studies corroborate the results in Table 1, where high recovery extents were obtained for LDPE at 85°C, HDPE at 110°C, and PP at 135°C using Xylene.

Finally, PET is insoluble in common solvents such as water, diethyl ether, and many typical organic solvents. In fact, PET is commonly recycled using glycol in a process called glycolysis [31]. However, the solvent-based dissolution–precipitation method for waste PET is emerging as a strategic approach for PET recovery. Chaudhari et al. [8] recycled PET using gamma-valerolactone as the solvent, while Ali et al. [32] found that phenol could dissolve PET plastic bottles, supported by the findings of Jalani et al. [26]. Due to the specific properties of PET, based on the series of conditions used, it was determined that it can be dissolved only using HFIP.

3.2 | Machine Learning

The first results attained by the ML portion were the optimal parameters obtained using Grid Search techniques. The best model was a Random Forest using the Gini Criterion (measures the quality of a split), Square Root Maximum Features (strategy used to find the maximum number of features in a split) and 100 trees for parameters. This model achieved a training accuracy of 92.03% and a testing accuracy of 84.62%; however, looking at other, often more meaningful metrics—Precision, Recall, and F1-Measure—the results suggest that the model was not as good

as initially thought, with the model having 42.31%, 50%, and 45.83% respectively. These results indicate lower confidence in the model's performance and its ability to properly generalize in unseen data. Although the accuracy appears satisfactory, it is crucial to recognize that the dataset is highly imbalanced. Further attempts using different algorithms, such as clustering methods, were carried out, having similar results.

To gain a better understanding of the data we were working with, we utilized t-SNE (t-distributed Stochastic Neighbor Embedding) [33] which facilitates the visualization of high-dimensional data in a 2D space. This is an iterative procedure that is highly nonlinear; as such, the axes are not meant to be interpreted quantitatively but merely as a visualization technique of how related the different data points are. In a t-SNE plot, the relative distances between points are crucial; neighboring points in the input space will typically remain neighbors in the low-dimensional representation [34].

The t-SNE plot is presented in Figure 1. In this case, each point is an attempt at dissolving a polymer using a given solvent. The points labeled as 1 had a solubility higher than 80% (blue dots) while the points labeled 0 had a solubility lower than 80% (red dots) and were considered a failure. Analyzing the resulting plot, it can be observed that a small cluster of positive data points are closely grouped, while the remaining positive points are scattered across the graph with no other positive neighbors. Having blue elements mixed with red elements implies that it is difficult to discriminate between both outcomes using the existing data and parameters. Notably, upon further examination, these closely situated points all belong to the same polymer, which was dissolved using different solvents. This observation suggests that, given the current dataset's structure and its limited size, it is challenging for a ML algorithm to generate reliable results. Enhancing the dataset—either by incorporating additional features (e.g., different temperatures) or increasing the number of data points, since we had to train and test with only 75 examples in total, would be advantageous [20] and could be a way to improve confidence in the model.

3.3 | Selective Extraction of Polymers From a Mixture of Polymers

Based on the preliminary solubility tests, the selective extraction of polymers from a mixture of polymers followed a similar procedure, described in Figure 2. The solubilities were determined using equation 1, the results being listed in Table 2.

The first step consisted of removing PS from the polymer mixture using Xylene at ambient temperature. As observed in the preliminary tests, Xylene proved to be a suitable solvent, achieving an extraction of approximately 99% for PS, both when isolated and within the mixture. Next, PVC was removed using THF. In the preliminary tests, THF demonstrated high solubility for both PS and PVC. However, since PS was already removed from the mixture, THF was only able to extract PVC. Again, this process achieved an extraction of approximately 94% for PVC, both when isolated and within the mixture. Afterward, TPU was removed using DMF. Similar to the previous case, DMF has high solubility for PS, PVC, and TPU. Yet, since PS and PVC

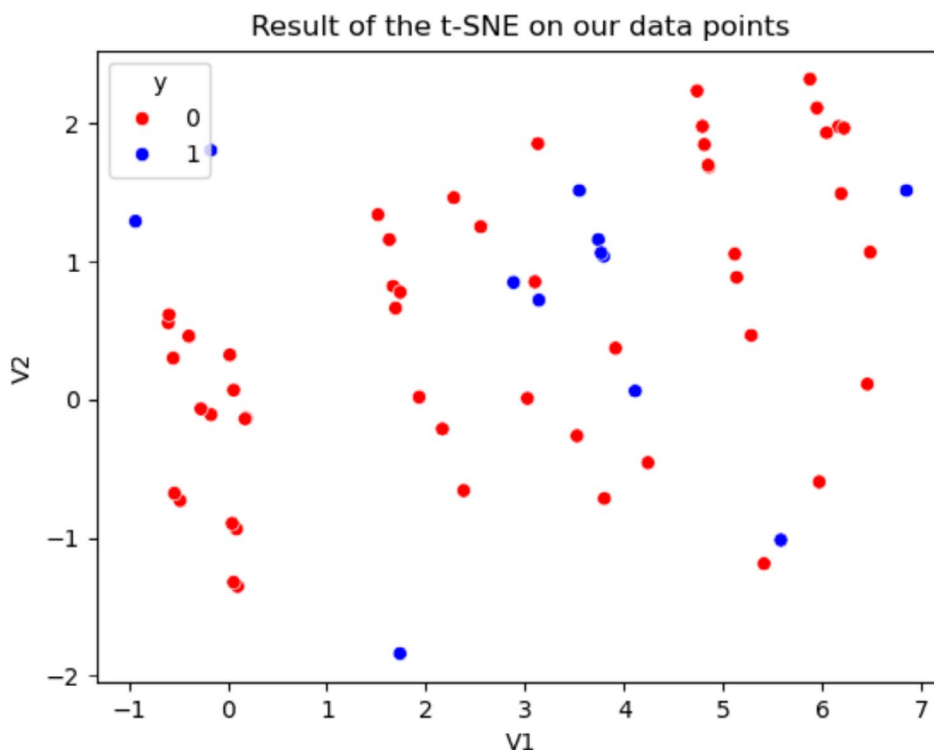


FIGURE 1 | Results of the t-SNE algorithm on the dataset built. The axes V1 and V2 are projections of the existing data dimensions, not necessarily linear relationships.

were no longer present in the mixture, DMF was suitable for extracting only TPU.

The next three polymers to be extracted were LDPE, HDPE, and PP. As mentioned, these polymers present low solubility in most solvents at room temperature. Therefore, based on literature, these polymers were extracted using Xylene at different temperatures: LDPE at 85°C, HDPE at 110°C, and PP at 135°C, with the extraction of 106%, 109%, and 104%, respectively. Although similar to the preliminary tests, the higher solubility extent observed in these steps may be attributed to the extraction of residual amounts of previously extracted polymers still in the mixture.

The remaining polymer in the mixture was PET. Preliminary tests showed that HFIP can easily dissolve PET. However, HFIP has low acute toxicity and is a strong irritant to skin and eyes, compromising the sustainability objectives of this work. Since PET was the only remaining polymer in the mixture, the final step of the procedure was not followed. Nonetheless, it was found that the remaining mass was approximately 99% of the original PET, consistent with preliminary observations.

Finally, it must be noted that some % solubility values exceed 100%. As shown in Table 1, a particular solvent may have the capacity to dissolve different polymers, even if only to a limited extent. This results in small amounts of different types of polymers being removed along with the target polymer, leading to yields exceeding 100%. Yet, overall, the % solubility is merely 100%. This is comparable with similar studies present in the literature. As an example, Walker et al. [12] recycled multilayer plastic packaging materials using solvent-targeted recovery and

precipitation, reporting that nearly 100% of the material was recovered. Similarly, Sánchez-Rivera et al. [19] recycled up to 10 polymers from post-industrial mixed plastic waste through precipitation principles, demonstrating a solvent selection approach capable of separating unknown plastic materials into purer components.

As observed, the proposed procedure successfully achieved accurate extraction extents of polymers from the mixture. Nonetheless, to further evaluate this methodology, the extracted polymers were analyzed using spectroscopy techniques as well as thermomechanical analysis. The FTIR, Raman, ¹³C NMR, and XRD spectra are shown in Figure 4, a detailed discussion of each analysis provided in the Supporting Information.

From Figure 3, it can be observed that, overall, all recycled polymers present a similar chemical structure to their virgin counterparts, though minor differences are detected.

Unlike the virgin PS (PSv), the recycled PS (PSr) FTIR spectrum (Figure 3a) shows a peak at 1700 cm⁻¹, commonly attributed to C=O stretching vibrations. This suggests that some of the PVC plasticizer could be removed from the polymer mixture along with PS. In fact, in the region between 3500 and 3200 cm⁻¹ of the PVC samples, attributed to O-H groups of the plasticizer, it can be observed that these groups are present in the virgin sample but absent in the recycled sample. This absence corroborates the partial removal of the plasticizer. Additionally, the peak at 1375 cm⁻¹, attributed to symmetric CH₃ deformations, present in the recycled HDPE (HDPEr), suggests some contamination with PP. However, all these contaminations appear to be minimal, as no differences are detected in the Raman spectra

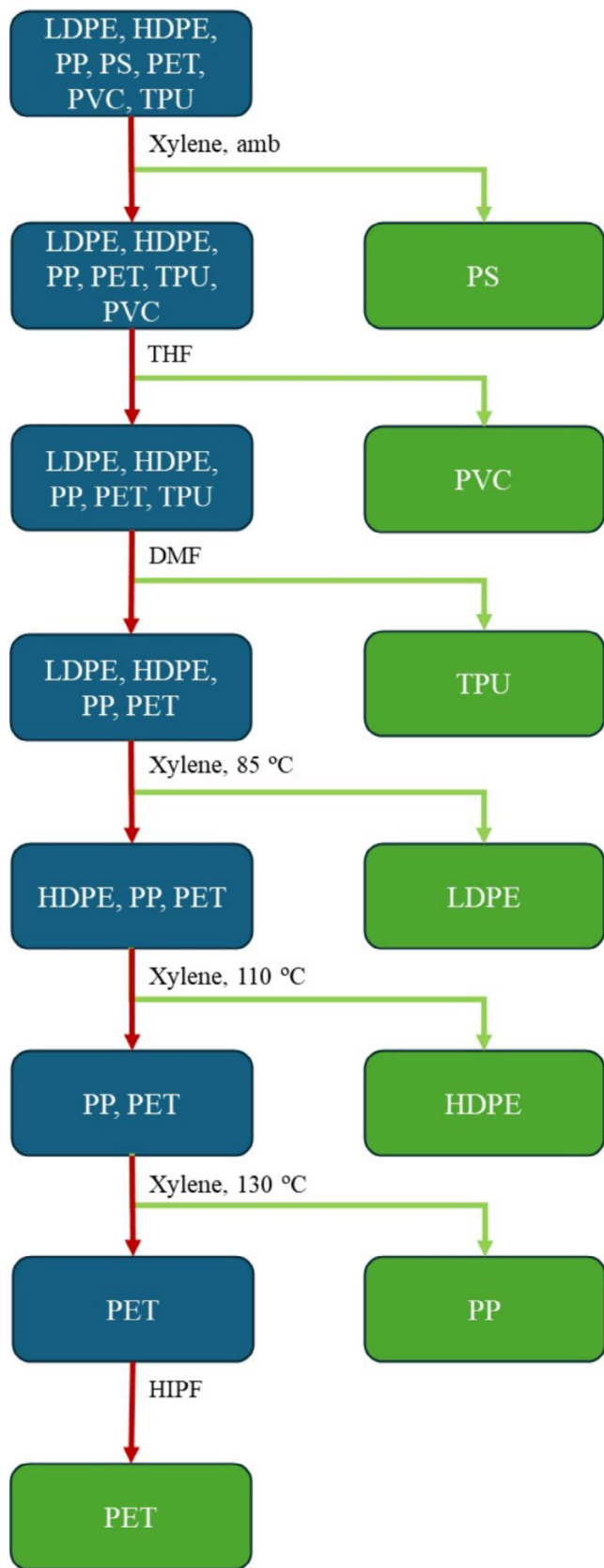


FIGURE 2 | Flowchart of the selective polymer extraction from the mixture of polymers.

TABLE 2 | Selective extraction of polymers from a mixture of polymers.

Polymer	% Solubility
PS	98.7% ± 4.1%
PVC	93.5% ± 6.4%
TPU	94.2% ± 3.9%
LDPE	106.1% ± 2.6%
HDPE	108.7% ± 6.4%
PP	104.1% ± 4.5%
PET	99.2% ± 4.7%

(Figure 3b). Similarly, the observations of ^{13}C NMR spectra (Figure 3c) indicate that despite the recycling process, the major structural features observed in the original polymers are largely retained in the recycled counterparts.

Regarding the XRD spectra, the results shown in Figure 3d indicate that PS, TPU, and PVC samples display a broad diffuse peak at 20° , signifying their amorphous nature. Both PS and PVC are widely recognized as amorphous polymers [35]. In contrast, the crystallinity of TPU depends on its composition, specifically influenced by its soft and hard segments [36]. In turn, LDPE, HDPE, PP, and PET are known for being crystalline polymers [35]. This is improved by the XRD patterns of polyolefin polymers (LDPE, HDPE, and PP) revealing well-defined peaks, demonstrating their crystalline nature. Likewise, the PET spectrum exhibits a broad pattern with faint peaks, indicating its partially crystalline structure.

In addition to spectrochemical analysis, the thermomechanical and thermal stability performance of the polymers was determined. In Figure 4, the DSC, DMA, and TGA results are presented, with detailed discussion available in the Supporting Information.

Analyzing the DSC thermograms presented in Figure 4a, it is evident that PS and PVC lack well-defined melting points (T_m), unlike LDPE, HDPE, PP, and PET. Hence, based on XRD and DSC results, PS and PVC are identified as amorphous polymers, while LDPE, HDPE, and PP are crystalline, which corroborates the XRD analysis. In contrast to the XRD spectrum of TPU, which suggested that this material is amorphous, a T_m is identified from DSC indicating that this material is at least partially crystalline. Finally, the PET thermograms do not exhibit well-defined peaks; hence, they can be classified as moderately crystalline. Further examination of the thermal events presented in Supporting Information reveals that the thermal characteristics of both virgin and recycled polymers are identical, except for the glass T_g of PS samples. Nelson et al. [37] studied the effects of recycling on PS shape memory polymers for in situ resource utilization. In contrast to the results presented in Figure 4, it was reported that the T_g of

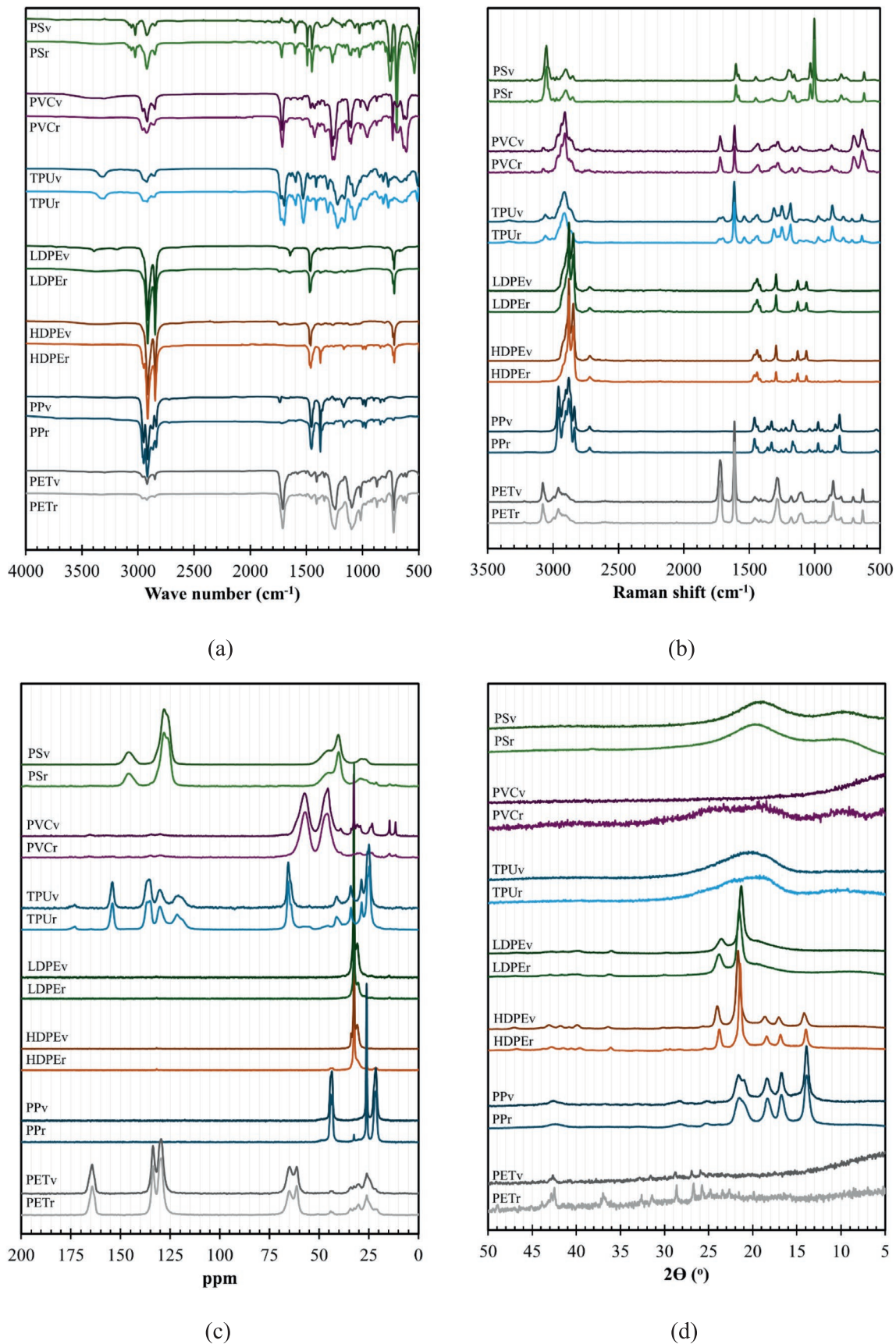


FIGURE 3 | Spectroscopy analyzes of virgin and recycled polymers: FTIR (a), Raman (b), ¹³C NMR (c) and XRD (d).

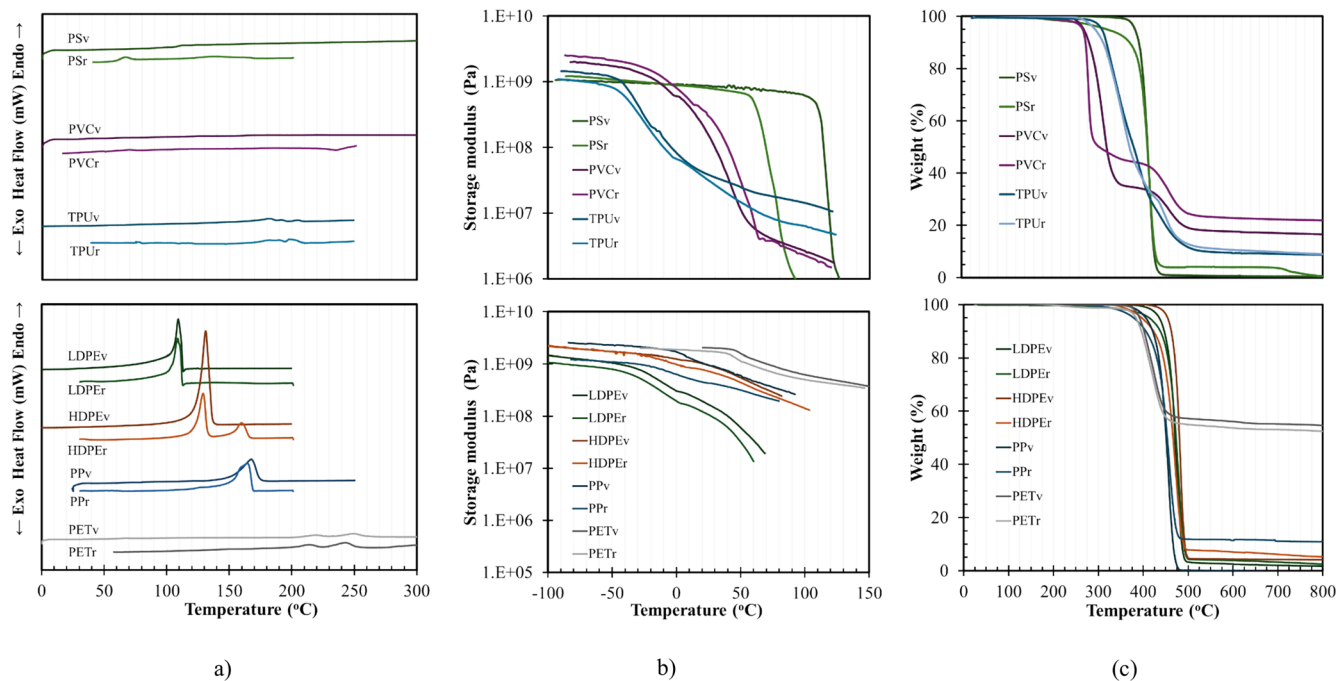


FIGURE 4 | Thermal properties of initial and recycled polymers: DSC (a), DMA (b) and TGA (c).

recycled polymers increased after 1 up to 6 extrusion cycles, attributing this to induced degradation. However, Momanyi et al. [38] analyzed the thermomechanical properties of recycled thermoplastics and found a decrease in the T_m of PP after recycling due to structural reorganization after melting. This could also explain the behavior observed in the PS samples presented in Figure 4.

Upon analyzing the thermomechanical properties of polymers, it is evident that recycled polymers exhibit identical modulus values when compared to their virgin counterparts. The exception is the PP samples, where the recycled version shows a slightly lower modulus at 25°C, which can be attributed to the structural reorganization after melting, as previously discussed. Additionally, examining the thermal characteristics (presented in Supporting Information) of both virgin and recycled polymers, it can be concluded that they are identical, except for the glass T_g of PS samples, corroborating the DSC analysis.

Finally, analyzing the TGA results, it can be observed that the recycled polymers exhibit similar thermal stability compared to their virgin counterparts, as the temperatures at which 10% mass loss occurs are identical for both virgin and recycled polymers. PSr exhibited a similar decomposition profile, though with a slightly pronounced early mass loss at lower temperatures (160°C). In a similar manner, the recycled PVC sample presented higher residual mass at 800°C. These observations can be attributed to three factors: (i) residual solvent entrapped within the polymer; (ii) alterations in the molecular structure, such as changes in crystallinity, due to the dissolution/precipitation process; (iii) some of the PVC plasticizer was removed at this stage [39]. Nonetheless, all samples show thermal stability well above their processing and use temperatures.

4 | Conclusions

This study aimed to reduce the environmental impact of the plastic sector by developing a recycling methodology that promotes polymer recovery through eco-friendly means. The principle of dissolution-precipitation was employed to selectively isolate polymers from a mixture, where the solubility parameters of the polymers and solvents, along with the dissolution obtained from the dissolution of individual polymers, were used to develop machine learning (ML) models. Although a training accuracy of 92.03% and a testing accuracy of 84.62% were achieved, the resulting models demonstrated Precision, Recall, and F1-Measure scores of 42.31%, 50%, and 45.83%, respectively. This was attributed to a cluster of positive data points being closely grouped, all belonging to the same polymer, which had been dissolved using different solvents. This suggests that the current dataset's structure and its limited size are challenging for an ML algorithm to produce reliable results. Nonetheless, this stage was instrumental in developing a methodology capable of isolating all polymers in a mixture with high selectivity (between 93.5% and 108.7%). The recovered polymers exhibited identical chemical, thermal, and mechanical properties to their original counterparts. Although additional data is needed to enhance the quality of the machine learning outputs and to incorporate greener solvents, this work provides a pathway toward a more sustainable and circular approach to plastic waste management.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.